Templated Synthesis of Aluminum Nanoparticles - A New Route to Stable Energetic Materials

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Nanoscale structural cavities in ionomer membrane films were used as templates for the facile synthesis of small aluminum nanoparticles via catalytic decomposition of an alane precursor. The loading of reactive aluminum in the composite film could be varied, up to more than half of the film weight. While the embedded nanoparticles were protected by the membrane structure from any significant oxidation for the composite films to exhibit surprising stability in ambient air, they could be fully accessed in base water for the hydrogen production quantitatively. The templated synthesis may represent a new route for stable aluminum nanoparticles and related energetic nanomaterials.

Introduction

Reactive nanoparticles as energetic materials have received much recent attention for a variety of existing and/or potential applications.[1,2] Among more extensively investigated are nano-sized (sub-100 nm) aluminum (Al) particles.[3−6] Their large specific surface area and energy density, when coupled or mixed with oxidative species, make them unique combustible additives in propellant formulations.[7] Nanoscale Al particles are also studied as high-capacity hydrogen storage materials.[8] Therefore, significant effort has been made on the development of synthetic methodologies for Al nanoparticles of desired properties.[3−6,9,10]

The chemical route based on thermal and/or catalytic decomposition of alane in the presence of a surface passivation agent for particle protection and stabilization has been identified as being particularly promising. The passivation agent for Al nanoparticles could be a metal coating[9a] or organic molecules such as perfluorinated carboxylic acids,[3,5] which could also serve as an oxidant source under energetic conditions. This method has generally yielded Al particles of 50−200 nm in average sizes, though smaller particles have been obtained recently in sonochemical environment with oleic acid as the surface passivation agent.[4] Ideally, very small Al nanoparticles (thus an extremely high surface area) of a narrow size distribution are desired for their distinctive advantages in energetic materials or for more effective hydrogen generation, but their bulk production in a consistent fashion and their protection for stability under ambient conditions present special challenges.

Here we report the use of nanoscale cavities in perfluorinated ionomer membrane as templates for the facile synthesis of small Al nanoparticles (diameters on the order of 10 nm) via catalytic decomposition of an alane precursor. While hosted in the cavities, for which the perfluorinated membrane structures should phenomenologically serve the same passivation function and also as a source of oxidant under energetic conditions, the Al nanoparticles were found to be mostly stable in ambient air. The effective hydrogen generation by the nanoparticles was used to determine the reactive Al content in the Al-in-membrane composite.

Results and Discussion

Nafion-117 membrane film supplied by DuPont Co. was purified and converted to the sodium form in a previously established procedure.[11] In the experiment for Al nanoparticles, a piece of the Nafion film was soaked in an isopropanol solution of $Ti(OC_3H_7)_4$ (0.5 M) at 80 °C for 12 h. Then, the film was rinsed repeatedly with isopropanol and acetone to clean the film surface, followed by drying under vacuum at 80 °C. In a glovebox under nitrogen atmosphere, the dry film containing the titanium salt was immersed in a tetrahydrofuran (THF) solution of 1-methylpyrrolidine alane (0.5 or 1 M) with stirring for 12 h, during which the film color turned black, consistent with the formation of small Al nanoparticles. The film was thoroughly washed with THF, dried under vacuum, and then characterized by using a series of techniques.

The X-ray powder diffraction patterns of the Al-in-Nafion composite films matched well with the face-centered-cubic (fcc) standard for bulk Al, but the peaks were generally broad (Figure 1), consistent with the embedded Al particles being nanoscale. The peak broadening was used to estimate the average particle size in terms of the Debye−Scherrer equation.[12] For the Al nanoparticles in Nafion films synthesized with alane concentra-
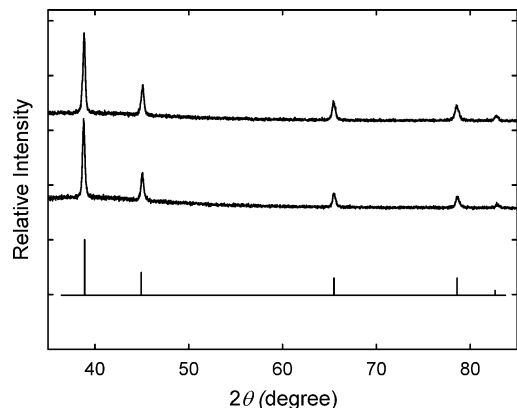
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Figure 1. X-ray diffraction patterns of the Al-in-Nafion films prepared with alane solution concentrations of 0.5 M (bottom) and 1 M (top) are compared with that of bulk fcc aluminum in JCPDS database.

tions of 0.5 and 1 M, the average particle sizes thus estimated were 13 and 15 nm, respectively.

Transmission electron microscopy (TEM) analyses of specimens from microtome allowed a cross-sectional view of the Al-in-Nafion films for the embedded nanoparticles. The specimens were prepared by cutting the films into ultrathin slices (on the order of 90 nm in thickness) in an ultramicrotome with a diamond knife, and then placing the slices on copper grids. Shown in Figure 2 is a representative TEM image on the specimen from the film prepared with the alane concentration of 0.5 M. A statistical analysis of the randomly dispersed Al nanoparticles in this and other images yielded an average particle size of 11 nm in diameter and a size distribution standard deviation of 2.5 nm (Figure 2). The particle sizes according to TEM, while more direct and thus accurate, are not so different from the relatively rough estimate in terms of the Debye–Scherrer equation described above. The energy dispersive X-ray (EDX) analysis of the specimen confirmed the presence of large amounts of Al and fluorine (a part of the Nafion membrane structure) and a small amount of titanium from the catalyst. However, there was only a negligible amount of oxygen in the specimen despite the fact that the EDX analysis was performed under ambient conditions, suggesting that the embedded Al nanoparticles were protected by the membrane structure from any significant oxidation.

At a higher resolution in the TEM imaging of the same Al-in-Nafion specimen, the crystal lattice fringes of individual Al nanoparticles embedded in the film could be observed (Figure 3). The majority of the nanoparticles appeared crystalline, consistent with the X-ray diffraction results presented above, and the lattice fringes were generally of a 0.235 nm spacing, corresponding to the (111) planes for Al. Thus, the structural cavities in Nafion membrane apparently served as templates for crystalline Al nanoparticles, for which the high crystallinity might be attributed to the progressive particle formation process inside the cavities. The overall process likely involved the alane in solution being transported into the cavities for catalytic decomposition, so that the amount of Al nanoparticles in the Nafion membrane was dependent on the alane solution concentration. However, as observed in previous studies on the formation of other nanoparticles in Nafion membrane,[13,14] significant variations in the amount of embedded materials in the membrane changed primarily the population of the nanoparticles, but affected much less on the sizes of the particles.

The Nafion membrane films could apparently host a substantial amount of Al nanoparticles, as demonstrated by the obvious
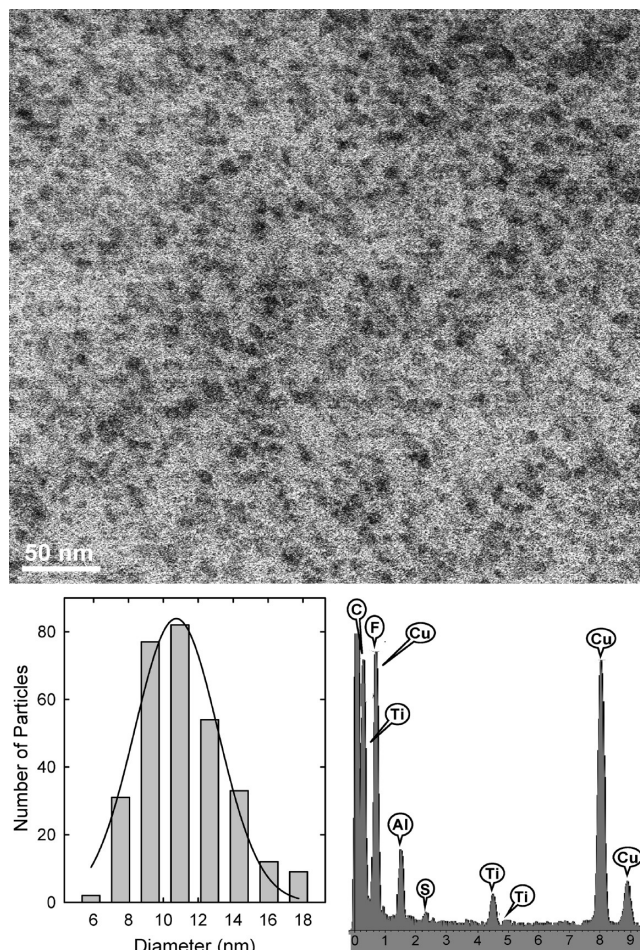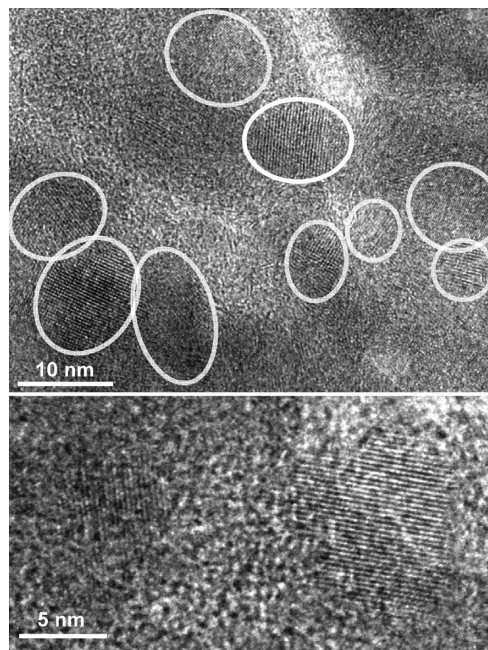

Figure 2. A representative TEM image for the specimen from ultramicrotome of the Al-in-Nafion film prepared with alane solution concentration of 0.5 M (top), a statistical size analysis of particles from multiple images (bottom right), and a corresponding EDX spectrum (bottom right).

weight increases of the films postalane reaction. For alane solutions of 0.5 and 1 M used in the reaction, the resulting films had weight increases of 14 and 29% (thus the implied Al contents in the films of 12 and 22%), respectively. The reactive Al contents in the films were determined by using the films to generate hydrogen gas in a basic aqueous solution.[15] The experiments were performed in a commercially supplied apparatus to allow accurate volumetric measurements of the hydrogen gas generated for the calculation of the reactive Al contents. The amounts of Al nanoparticles in the two films thus determined were 11 and 20% of the film weights, in reasonable agreement with the observed weight increases postalane reaction discussed above.

The population of Al nanoparticles in the Nafion membrane could be further increased by using more concentrated alane solutions in the reaction. For example, the reaction of the dry Nafion membrane film (containing the same titanium salt) in a more concentrated alane solution (2 M) under otherwise the same experimental conditions, the film weight increase was 122% (thus the implied Al content of 55%). Both the thermogravimetric analysis (TGA) and hydrogen generation results suggested that the weight increase was due to the amount of reactive Al in the film (reactive Al being 54–57% of the film weight in repeated TGA and hydrogen generation measurements). X-ray diffraction analysis of the Al-in-Nafion composite film yielded the characteristic pattern for nanoscale Al, very

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Figure 3. Representative high-resolution TEM images for the specimen from ultramicrotome of the Al-in-Nafion film prepared with alane solution concentration of 0.5 M.
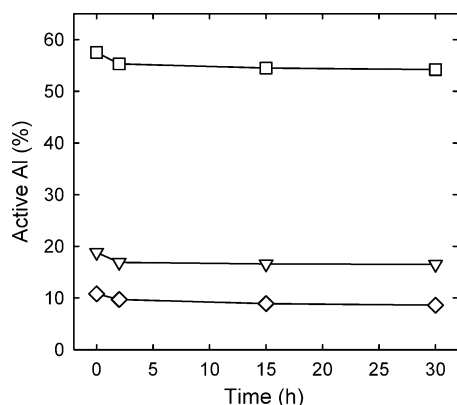
Figure 4. The reactive Al contents in the various Al-in-Nafion films (based on volumetric measurements of the hydrogen gas generated) over time in ambient air.

similar to those shown in Figure 1. The estimated average Al particle diameter was 17 nm in terms of the same Debye−Scherrer equation calculation, slightly larger than those of the other samples discussed above. The composite film was very brittle, making the cross-sectional slicing in ultramicrotome rather challenging. Nevertheless, the TEM images of the slices obtained anyway generally suggested that the film was packed with nanoparticles, which might have contributed to the difficulty in the ultramicrotome operation.

All of the Al-in-Nafion film samples were surprisingly stable in ambient air, with the reactive Al contents changed only marginally over time (Figure 4). The relatively more significant initial decrease in the reactive Al content might be attributed to the oxidation of the Al nanoparticles close to the film surface. The small sacrifice of these nanoparticles due to the oxidation probably "sealed off" the composite film as a whole, minimizing any subsequent oxidation. The Nafion membrane structure was apparently not permeable to oxygen under the ambient air conditions, preventing any substantial oxidation of the embedded Al nanoparticles. On the other hand, the Al nanoparticles were fully accessible under the hydrolysis conditions for the nearly

quantitative generation of hydrogen gas. Therefore, the Al-in-Nafion composite films may serve as a unique platform for stable energetic materials and/or as materials for energy storage.

The Nafion membrane films embedded with Al nanoparticles, especially those with high loadings, could be crushed via grinding in a mortar to form black-gray powdery materials. These materials could subsequently be dispersed in solvents such as hexane with sonication, though the resulting suspension was unstable (with significant precipitation within a few minutes). Interestingly, however, the Al nanoparticles were largely unaffected in the process, maintaining their sizes and dispersion according to electron microscopy and X-ray diffraction results. Thus, one might consider these powders as essentially Al nanoparticles protected and stabilized by Nafion polymers (disintegrated backbones in the original membrane film).

It is known that the structural cavities in ionomer membranes represented by Nafion films resemble those in reverse micelles.[16,17] According to modeling results the cavities should be small (around 4 nm in average diameter) and interconnected by channels. Experimentally, however, larger metal and metal salt (such as Ag and Ag_2S, respectively) nanoparticles were readily prepared in Nafion membrane films, with sizes generally averaging 10−15 nm and of relatively narrow size distributions.[13,14] Those results were consistent with a proposed mechanistic picture in which the cavities and channels could be rearranged (such as the channel connecting two cavities being squeezed out for a larger cavity) to accommodate the growth of the nanoparticles toward their thermodynamically and/or kinetically preferred sizes, but only up to a limit imposed by the much more rigid perfluorinated polymer backbones in the membrane films.[16,17] The results on Al nanoparticles reported here seem to be consistent with the same proposed mechanistic picture. There were no dramatic increases in average particle sizes even at very high Al loadings. On the other hand, the high loadings of Al nanoparticles probably strained the membrane films so severely to make them vulnerable to decomposition (via grinding in a mortar, for example, as discussed above).

In summary, the results in this work have demonstrated that the structural cavities in ionomer membrane films could serve as ideal templates for facile production of well-dispersed small Al nanoparticles. The membrane structure could apparently protect the embedded Al nanoparticles from any significant oxidation, which made the reactive Al-in-Nafion composite films surprisingly stable in ambient air. On the other hand, the Al nanoparticles could be used to produce hydrogen from water in a nearly quantitative fashion. The ability to incorporate a larger amount of reactive Al into Nafion membrane (up to more than 50% by weight in the resulting composite film) is fundamentally interesting and potentially technologically valuable, though a clear understanding of the structures in these composite films of very high Al loadings requires more investigations. The templated synthesis may represent a new route for stable Al nanoparticles and related energetic nanomaterials.

Experimental Section

Materials. Lithium aluminum hydride ($LiAlH_4$), anhydrous aluminum chloride ($AlCl_3$), titanium(IV) isopropoxide, and 1-methylpyrrolidine were supplied by Sigma-Aldrich. The solvents diethyl ether, THF, and hexane were carefully dried and freshly distilled over sodium metal before use. The 1-methylpyrrolidine alane, $H_3AlN[(C_4H_8)(CH_3)]$, was prepared according to the previously reported procedure.[5,18] The com-

pound as a transparent liquid was characterized by NMR methods and confirmed unambiguously.

Nafion-117 membrane films (DuPont Co.) were purified/cleaned and converted to the sodium form by using procedures already well-established in the literature.[11] First, the films were immersed in concentrated nitric acid and stirred at 60 °C for 24 h. The acid was decanted, and the films were immersed sequentially in aqueous solutions of 60, 40, and 20% nitric acid, each for 1 h with stirring, followed by washing thoroughly with deionized water. The Nafion films thus treated were clear and optically transparent down to 200 nm. The conversion to the sodium form was accomplished by soaking the cleaned Nafion films in a 0.1 M aqueous sodium hydroxide solution with stirring for 24 h, followed by washing thoroughly with deionized water until neutral. The films in the sodium form remained equally clear and optically transparent.

Measurements. NMR spectra were measured on a JEOL Eclipse +500 NMR spectrometer or a Bruker Advance 500 NMR spectrometer. X-ray powder diffraction measurements were performed on a Scintag XDS-2000 powder diffraction system. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA851e or a TA Instruments Q500 TGA system. Electron microscopy imaging was conducted on a Hitachi HD-2000 scanning transmission electron microscopy (S-TEM) system (TEM and Z-contrast modes) and a Hitachi H-9500 TEM system, and the energy dispersive X-ray (EDX) analysis was performed in situ on the same S-TEM system. In the preparation for TEM specimen by the cross-sectional slicing of a film, an Ultracut-E microtomy equipped with a diamond knife was used.

A commercially supplied glass apparatus (Quark Glass, Vineland, New Jersey) was used for the accurate volumetric measurement of the hydrogen gas generated by the reactive Al in hydrolysis.[19] The apparatus was first calibrated with magnesium as the reactive metal. Small magnesium pieces around 3 mg (accurately weighted) were each added to a dilute hydrochloric acid solution in the apparatus, and the corresponding volumes of hydrogen gas thus generated in the apparatus were measured. The averaged results suggested ~1% accuracy for the apparatus. In a typical measurement for reactive Al, a piece of the Al-in-Nafion film (around 30 mg, accurately weighted) was added to an aqueous sodium hydroxide solution (0.5 M) in the apparatus, and the resulting hydrogen gas volume was determined for the calculation of the reactive Al content in the film.

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